U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-258 365

Assessment of Adipic Acid as a Potential Air Pollution Problem. Volume XIII

GCA Corp, Bedford, Mass GCA Technology Div

Prepared for

Environmental Protection Agency, Research Triangle Park, N C

Jan 76

BEST SELLERS

FROM NATIONAL TECHNICAL INFORMATION SERVICE

NTIS

Product Liability Insurance: Assessment of Related Problems and Issues. Staff Study
PB-252 204/PAT 181 p PC$9.50/MF$3.00

Evaluation of Home Solar Heating System
UCRL-51 711/PAT 154 p PC$6.75/MF$3.00

Developing Noise Exposure Contours for General Aviation Airports
ADA-023 429/PAT 205 p PC$7.75/MF$3.00

Cooling Tower Environment, 1974. Proceedings of a Symposium Held at the University of Maryland Adult Education Center on Mar. 4-6, 1974
CONF-74 0302/PAT 648 p PC$13.60/MF$3.00

Biological Services Program. Fiscal Year 1975
PB-251 738/PAT 52 p PC$4.50/MF$3.00

An Atlas of Radiation Histopathology
TID-26-676/PAT 234 p PC$7.60/MF$3.00

Federal Funding of Civilian Research and Development. Vol. 1. Summary
PB-251 266/PAT 61 p PC$4.50/MF$3.00

Federal Funding of Civilian Research and Development. Vol. 2. Case Studies
PB-251 683/PAT 336 p PC$10.00/MF$3.00

Handbook on Aerosols
TID-26-608/PAT 141 p PC$6.00/MF$3.00

for the Assessment of Ocean Outfalls
ADA-023 514/PAT 34 p PC$4.00/MF$3.00

Guidelines for Documentation of Computer Programs and Automated Data Systems
PB-250 867/PAT 54 p PC$4.50/MF$3.00

NOx Abatement for Stationary Sources in Japan
PB-250 586/PAT 116 p PC$5.50/MF$3.00

U.S. Coal Resources and Reserves
PB-252 752/PAT 16 p PC$3.50/MF$3.00

Structured Programming Series. Vol. XI. Estimating Software Project Resource Requirements
ADA-016 416/PAT 70 p PC$4.50/MF$3.00

Assessment of a Single Family Residence Solar Heating System in a Suburban Development Setting
PB-246 141/PAT 244 p PC$8.00/MF$3.00

Technical and Economic Study of an Underground Mining, Rubblization, and In Situ Retorting System for Deep Oil Shale Deposits. Phase I Report
PB-249 344/PAT 223 p PC$7.75/MF$3.00

A Preliminary Forecast of Energy Consumption Through 1985
PB-251 445/PAT 69 p PC$4.50/MF$3.00

HOW TO ORDER

When you indicate the method of payment, please note if a purchase order is not accompanied by payment, you will be billed an addition $5.00 *ship and bill* charge. And please include the card expiration date when using American Express.

Normal delivery time takes three to five weeks. It is vital that you order by number or your order will be manually filled, insuring a delay. You can opt for *airmail delivery* for a $2.00 charge per item. Just check the *Airmail Service* box. If you're really pressed for time, call the NTIS Rush Order Service. (703) 557-4700. For a $10.00 charge per item, your order will be airmailed within 48 hours. Or, you can pick up your order in the Washington Information Center & Bookstore or at our Springfield Operations Center within 24 hours for a $6.00 per item charge.

You may also place your order by telephone or TELEX. The order desk number is (703) 557-4650 and the TELEX number is 89-9405.

Whenever a foreign sales price is NOT specified in the listings, all foreign buyers must add the following charges to each order: $2.50 for each paper copy; $1.50 for each microfiche; and $10.00 for each Published Search.

Thank you for your interest in NTIS. We appreciate your order.

METHOD OF PAYMENT

- ☐ Charge my NTIS deposit account no._____
- ☐ Purchase order no._____
- ☐ Check enclosed for $_____
- ☐ Charge to my American Express Card account number

Card expiration date_____

Signature_____

☐ Airmail Services requested

NAME_____

ADDRESS_____

CITY, STATE, ZIP_____

Item Number	Quantity		Unit Price*	Total Price*
	Paper Copy (PC)	Microfiche (MF)		
			Sub Total	
			Additional Charge	
			Enter Grand Total	

All Prices Subject to Change
11/76

Clip and mail to:

NTIS

National Technical Information Service
U.S. DEPARTMENT OF COMMERCE
Springfield, Va. 22161
(703) 557-4650 TELEX 89-9405

282049

PB 258 365
GCA-TR-75-32-G (13)

ASSESSMENT OF ADIPIC ACID AS A POTENTIAL AIR POLLUTION PROBLEM

VOLUME XIII

FINAL REPORT

Contract No. 68-02-1337
Task Order No. 8

Prepared For
U.S. ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park
North Carolina 27711

January 1976

GCA/TECHNOLOGY DIVISION
BEDFORD, MASSACHUSETTS 01730

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
GCA-TR-75-32-G(13)		

4. TITLE AND SUBTITLE

Assessment of Adipic Acid as a Potential Air Pollution Problem

5. REPORT DATE: January 1976

6. PERFORMING ORGANIZATION CODE:

7. AUTHOR(S)

Robert M. Patterson Eric Garshick
Mark I. Bornstein

8. PERFORMING ORGANIZATION REPORT NO.:

9. PERFORMING ORGANIZATION NAME AND ADDRESS

GCA Corporation
GCA/TECHNOLOGY DIVISION
Bedford, Massachusetts

10. PROGRAM ELEMENT NO.:

11. CONTRACT/GRANT NO.: 68-02-1337

12. SPONSORING AGENCY NAME AND ADDRESS

Environmental Protection Agency
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

13. TYPE OF REPORT AND PERIOD COVERED: Final

14. SPONSORING AGENCY CODE:

15. SUPPLEMENTARY NOTES:

16. ABSTRACT

This report is one of a series which assesses the potential air pollution impacts of 14 industrial chemicals outside the work environment. Topics covered in each assessment include physical and chemical properties, health and welfare effects, ambient concentrations and measurement methods, emission sources, and emission controls. The chemicals investigated in this report series are:

Volume I	Acetylene	Volume VIII	Formaldehyde
Volume II	Methyl Alcohol	Volume IX	Methyl Methacrylate
Volume III	Ethylene Dichloride	Volume X	Ortho-Xylene
Volume IV	Benzene	Volume XI	Maleic Anhydride
Volume V	Acetone	Volume XII	Dimethyl Terephthalate
Volume VI	Acrylonitrile	Volume XIII	Adipic Acid
Volume VII	Cyclohexanone	Volume XIV	Phthalic Anhydride

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT: Unlimited

19. SECURITY CLASS *(This Report)*: Unclassified

21. NO. OF PAGES: 22

20. SECURITY CLASS *(This page)*: Unclassified

22. PRICE: 3.50

EPA Form 2220-1 (9-73)

PRICES SUBJECT TO CHANGE

GCA-TR-75-32-G(13)

ASSESSMENT OF ADIPIC ACID AS A POTENTIAL AIR POLLUTION PROBLEM

Volume XIII

by

Robert M. Patterson
Mark I. Bornstein
Eric Garshick

GCA CORPORATION
GCA/TECHNOLOGY DIVISION
Bedford, Massachusetts

January 1976

Contract No. 68-02-1337
Task Order No. 8

EPA Project Officer
Michael Jones

EPA Task Officer
Justice Manning

U.S. ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park
North Carolina 27711

This report was furnished to the U.S. Environmental Protection Agency by the GCA Corporation, GCA/Technology Division, Bedford, Massachusetts 01730, in fulfillment of Contract No. 68-02-1337, Task Order No. 8. The opinions, findings, and conclusions expressed are those of the authors and not necessarily those of the U.S. Environmental Protection Agency or of the cooperating agencies. Mention of company or product names is not to be considered as an endorsement by the U.S. Environmental Protection Agency.

ABSTRACT

This report is one of a series which assesses the potential air pollution impacts of 14 industrial chemicals outside the work environment. Topics covered in each assessment include physical and chemical properties, health and welfare effects, ambient concentrations and measurement methods, emission sources, and emission controls. The chemicals investigated in this report series are:

Volume I	Acetylene
Volume II	Methyl Alcohol
Volume III	Ethylene Dichloride
Volume IV	Benzene
Volume V	Acetone
Volume VI	Acrylonitrile
Volume VII	Cyclohexanone
Volume VIII	Formaldehyde
Volume IX	Methyl Methacrylate
Volume X	Ortho-Xylene
Volume XI	Maleic Anhydride
Volume XII	Dimethyl Terephthalate
Volume XIII	Adipic Acid
Volume XIV	Phthalic Anhydride.

CONTENTS

		Page
Abstract		iii
List of Tables		v
Sections		
I	Summary and Conclusions	1
II	Air Pollution Assessment Report	3
	Physical and Chemical Properties	3
	Health and Welfare Effects	4
	Ambient Concentrations and Measurements	5
	Sources of Adipic Acid Emissions	8
	Adipic Acid Control Methods	10
III	References	12
Appendix		
A	Adipic Acid Manufacturers	14

TABLES

No.		Page
1	Significant Properties of Adipic Acid	3
2	Estimated Adipic Acid Consumption	8
3	Sources and Emission Estimates of Adipic Acid	9
4	Scrubber	11
5	Cyclones	11

SECTION I

SUMMARY AND CONCLUSIONS

Adipic acid is an odorless, white crystalline powder which is manufactured by the catalytic oxidation of cyclohexane, with cyclohexanone and cyclohexanol as intermediates. Its primary use is in the production of polyamide fibers and plastics.

Adipic acid dust in air may irritate mucous membranes and may cause dermatitis. When ingested it is no more toxic than common food acids such as citric acid, and it is used as a baking powder ingredient and as a food additive. The main hazard in air is the possibility of dust explosions, and the lower explosive limit is 10 to 15 g/m^3.

Simple diffusion modeling estimates place the likely maximum 1-hour average ambient concentration at about 0.67 mg/m^3 (0.11 ppm), and 0.37 mg/m^3 (0.062 ppm) for a 24-hour average. There is no NIOSH recommended occupational standard.

About 1.5 billion pounds of adipic acid were produced in 1974, and production is expected to increase about 7 percent per year for the next several years. The primary emission sources are production and end-product manufacture. Total emissions are estimated to have been 1.5 million pounds in 1974.

Emission control methods currently in use and their efficiencies are:

- Scrubbers 90 percent
- Cyclones 93.8+ percent
- Bag filters Almost 100 percent

Based on the results of the health effects research presented in this report, and the ambient concentration estimates, adipic acid as an air pollutant apparently does not pose a threat to the health of the general population. In addition, adipic acid does not appear to pose other environmental insults which would warrant further investigation or restriction of its use at the present time.

SECTION II

AIR POLLUTION ASSESSMENT REPORT

PHYSICAL AND CHEMICAL PROPERTIES

Adipic acid is an odorless, white crystalline powder. It is manufactured by the catalytic oxidation of cyclohexane with cyclohexanone and cyclohexanol as intermediates. Some adipic acid is used as a baking powder ingredient and as a food additive. Its main outlet is as a raw material for the production of polyamide fibers and plastics (nylon 6,6), and for resins used in electrical insulation and protective coatings.[1] Significant physical properties are presented in Table 1.

Table 1. SIGNIFICANT PROPERTIES OF ADIPIC ACID

Synonyms	Hexanedioic acid, 1, 4-butanedicarboxylic acid
Chemical formula	$COOH(CH_2)_4COOH$
Molecular weight	146.14
Boiling point	At 760 mm Hg 330°C with decomposition 100 mm Hg 265°C
Melting point	152°C
Specific gravity	1.360 (25°/4°C)
Vapor pressure	<1 mm Hg at 25°C 1 mm Hg at 159.5°C
Solubility	2.5 percent by weight at 25°C in water Soluble in alcohol
Lower explosive limit	10 to 15 g/m^3 dust in air
Ignition temperature	550°C (200 mesh particles)
Flash point	191°C (closed cup)
At 25°C and 760 mm Hg	1 ppm = 6 mg/m^3 1 mg/m^3 = 0.167 ppm

HEALTH AND WELFARE EFFECTS

Effects on Man

Adipic acid dust in air may act as an irritant on the mucous membranes of the lungs and nose. It has a drying action on the skin and may cause dermatitis. There have been no reports in the literature of injury during industrial usage. Exposure to adipic acid vapor is impossible at ambient conditions due to its low vapor pressure.

Adipic acid once ingested is no more toxic than common food acids such as citric acid. Humans were fed 100 mg/kg body weight for up to 8 days with no toxic effects.[2] No occupational exposure standard has been established, but its lower explosive limit of 10 to 15 g/m^3 of air must be noted.

Effects on Animals

Acute Poisoning - Adipic acid in animals, as in man, may act as a mucous membrane irritant. In rats, death has been caused by oral administration of 3,600 mg/kg body weight. In mice the oral LD_{50} is 1,900 mg/kg.[3]

Chronic Poisoning - Two male and two female rats were exposed to 126 mg/m^3 adipic acid dust for 6 hours daily for 15 days.[4] There were no toxic signs and all blood tests were normal. The animals were sacrificed, with an autopsy showing no changes in any organ. Female albino rats fed 1.0 percent adipic acid in their daily diet for 2 years showed no evidence of toxicity related to the compound. Male albino rats fed adipic acid at the 0.1, 1.0, 3.0, and 5.0 percent levels in the daily diet showed no ill effects, except at the 3.0 and 5.0 percent level a temporary retardation of growth was observed.[5]

Effects on Vegetation

The effects of adipic acid on vegetation have not been documented in the literature.

Effects on Materials

Violent chemical reactions may occur when adipic acid comes in contact with strong oxidizing agents.[1]

Other Effects

Decomposition - Heating above 330°C or prolonged heating at its melting point causes decomposition to cyclopentanone, n-valeric acid, and other compounds that are toxic to man and animals.[1]

Explosive Dust - The principal hazard associated with adipic acid in air is the danger of dust explosions[1,6,7] as with any organic powder.

AMBIENT CONCENTRATIONS AND MEASUREMENTS

Ambient Concentration Estimates

The largest installation for adipic acid production is located in a town of about 60,000 population, and it has a capacity of about 620 million lb/yr. Assuming a 0.05 percent loss, this converts to an emission rate of:

$$\frac{(0.0005 \text{ emission factor})\ (620 \times 10^6 \text{ lb/yr})\ (453.6 \text{ g/lb})}{3.1536 \times 10^7 \text{ sec/yr}}$$

$$= 4.5 \text{ g/sec of adipic acid.}$$

Some assumptions must be made regarding this adipic acid release to the atmosphere. First of all, the emissions do not all come from one source location, but rather from a number of locations within the plant. Thus, the emissions can be characterized as coming from an area source which will be taken to be 100 meters on a side. Secondly, the emissions occur at different heights, and an average emission height of 10 meters is assumed. Thirdly, it is assumed that these emissions are in the form of particulate small enough to behave as a gas (of the order of 10 μm).

Ground level concentrations can then be estimated at locations downwind of the facility.[8] To do this a virtual point source of emission is assumed upwind of the facility at a distance where the initial horizontal dispersion coefficient equals the length of a side of the area divided by 4.3. In this case:

$$\sigma_{yo} = 100\text{m}/4.3 = 23.3\text{m}$$

Assuming neutral stability conditions (Pasquill-Gifford Stability Class D) with overcast skies and light winds, the upwind distance of the virtual point source is approximately 310 meters. With consideration of the plant boundary, it is reasonable to assume that the nearest receptor location is thus about 500 meters from the virtual point source. Finally, taking 2 m/sec as an average windspeed, the ground level concentration may be calculated from:

$$\chi = \frac{Q}{u\pi\sigma_y\sigma_z} e^{-1/2\left(\frac{H}{\sigma_z}\right)^2}$$

or

$$\chi = \frac{4.5}{(2)\ \pi\ (36)\ (18.5)} e^{-1/2\left(\frac{10}{18.5}\right)^2}$$

$$= 0.93\ \text{mg/m}^3$$

for a 10-minute average concentration. Over a period o an hour this becomes 0.93 mg/m^3 (0.72) = 0.67 mg/m^3 1-hour average concentration. Over a 24-hour period, the average concentration might roughly be expected to be about 0.37 mg/m^3.

Measurement Techniques

Very limited data exist in the literature for the determination of adipic acid in air. Considerable attention has been given to the elution of free monobasic carboxylic acids. However, very limited work with dibasic acids has been performed. Because of the difficulties associated with the elution of these normally solid, high boiling point compounds, previous gas chromatograph analyses have been indirect. These methods have relied on preinjection treatments of the dibasic acid, consisting of either reduction to a glycol and/or esterification. The accuracy of these methods is very questionable, and they are time consuming.[9]

Studies have been performed on a more reliable method for the determination of adipic acid. In one technique adipic acid is determined by using a GC and a flame ionization detector without any preinjection treatment.[10] Adipic acid dissolved in dimethyl formamide is introduced into the GC column. The column is composed of 316 stainless steel (2 feet by 1/8 inch) packed with Porapak Q coated with 7 weight percent FFAP, terephthalic acid terminated carbowax 20 M, commonly referred to as "Free Fatty Acid Phase." This experiment was unfortunately only run on samples containing 5.9 to 25.0 weight percent adipic acid; however, excellent results were obtained. The sensitivity of this method implies that adipic acid can be determined in the parts per billion range.[11]

SOURCES OF ADIPIC ACID EMISSIONS

Adipic Acid Production and Consumption

The production of adipic acid in 1974 was 1,505 million pounds, and it is expected to increase at 6.9 percent per year for the next several years.[12] Approximately 90 percent of all adipic acid produced is used for the manufacture of nylon 6,6. Plasticizers, lubricants, and polyurethane resins consume an additional 8 percent of the total production. Five companies at 7 locations are presently manufacturing adipic acid. See Appendix A for names and locations. The consumption of adipic acid for final products is shown in Table 2.[13] Expected growth rates for each sector of the market are also shown in this table.

Table 2. ESTIMATED ADIPIC ACID CONSUMPTION - 1974[13]

	Million pounds	% annual growth
Nylon fibers	1301	7.3
Nylon resins	69	7.3
Plasticizers and lubricants	61	1.8
Polyurethane resins	58	1.8
Polyester resins	6	1.8
Food additives	8	1.8
Miscellaneous	2	0
	1505	6.9

Adipic Acid Sources and Emission Estimates

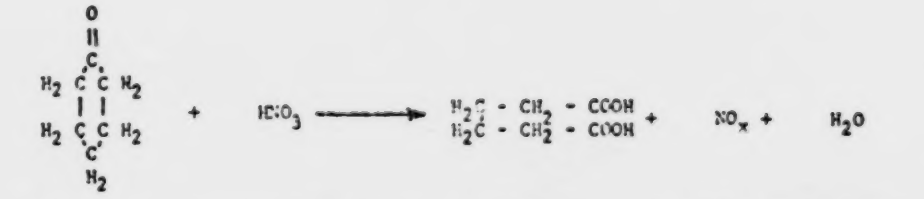
Primary sources of emissions of adipic acid result from adipic acid production and end product manufacture. Total emissions from both

categories are estimated to be 1.5 million pounds representing 0.1 percent of total production as shown in Table 3.

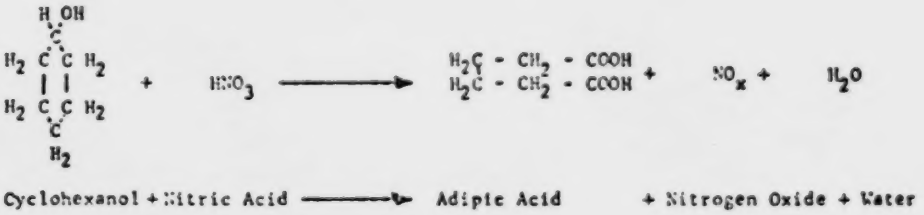
Table 3. SOURCES AND EMISSION ESTIMATES OF ADIPIC ACID

	Million pounds
Adipic acid production	0.75
End product manufacture	0.75
Total	1.50

Adipic acid is manufactured by reacting cyclohexanone/cyclohexanol with nitric acid. The following two equations illustrate the reactions involved.



Cyclohexanone + Nitric Acid ⟶ Adipic Acid + Nitrogen Oxide + Water



Cyclohexanol + Nitric Acid ⟶ Adipic Acid + Nitrogen Oxide + Water

In a recent study[14] on adipic acid manufacture it was reported that the only source of adipic acid emissions results from conveyors, driers, and melters. The emission factor reported was 0.0005 pounds of adipic acid lost per pound of adipic acid produced. Using this factor and the most recent production figure results in 0.75 million pounds of adipic acid emitted to the atmosphere from production.

Emissions from end product manufacture are similarly estimated to be 0.75 million pounds. Only trace quantities have been reported from the manufacturing of nylon 6,6, the major use of adipic acid.[15]

Storage losses are considered to be negligible because the final product is a solid and is not subject to evaporation. Any handling losses resulting from the storage of the final product are already included in the previously mentioned emission factor.

ADIPIC ACID CONTROL METHODS

Three types of control devices are currently being used by the industry to reduce emissions: scrubbers, cyclones and bag filters. In a recent study concerning the adipic acid industry, one plant is reportedly using a scrubber with an efficiency of approximately 90 percent. This system is used to control adipic acid dust generated from finished product operations. Two other plants using cyclones with efficiencies between 93.8 percent and 100 percent, and bag filters with efficiencies approaching 100 percent, have also been reported. Cost data for the various systems are presented in Tables 4 and 5. Complete data for the bag filter system, however, are not available. The only information which is available is the installed cost of $48,000.*

*Updated to first quarter 1975..

Table 4. SCRUBBER[a]

Scrubbing liquid rate	5 GPM
Design temperature	120°F
Gas rate	18,000 SCFM
Installed cost	$46,100
Annual operating cost	$ 4,600
Value of recovered product	0
Net operating cost	$ 4,600
Efficiency	90%

[a]Costs updated to first quarter 1975.

Table 5.[14] CYCLONES[a]

Installed cost	$51,200
Annual operating cost	$ 2,600
Value of recovered product	$ 4,345
Net operating cost	-$ 1,745
Efficiency	93.8%

[a]Costs updated to first quarter 1975.

SECTION III

REFERENCES

1. Adipic Acid. National Safety Council Data Sheet. National Safety Council, 425 North Michigan Avenue, Chicago. 1956.

2. Weizel, G. Zeitschrifte Physiologische Chemie. (Germany). 282:185-91. 1947.

3. The NIOSH Toxic Substances List 1974 Edition. HEW Publication No. (NIOSH) 74-134.

4. Gage, J. C. The Subacute Inhalation Toxicity of 109 Industrial Chemicals. Brit. J. Ind. Med. 27:1-18. 1970.

5. Hazelton Laboratory Reports dated August 20, 1952 and December 31, 1952 (unpublished data). Cited in Reference 1.

6. OSHA Material Safety Sheet. E. I. DuPont de Nemours & Company, Inc., 1007 Market Street, Wilmington. 1972.

7. OSHA Material Safety Sheet. Monsanto Company, 800 North Lindbergh Boulevard, St. Louis. 1972.

8. Turner, D. B. Workbook of Atmospheric Dispersion Estimates. U.S. Environmental Protection Agency, Report No. AP-26. April 1973.

9. Appleby, A., J. Mayre. Journal of Gas Chromatography, Vol. 5. 1967.

10. Gross, D., H. Tinker. Quantitative Gas Chromatographic Determination of Free Adipic Acid. Analytical Chemistry. January 1968.

11. Leithe, W. The Analysis of Air Pollutants. Ann Arbor-Humphrey Science Publishers. 1970.

12. U.S. Production of Selected Snythetic Organic Chemicals. United States International Trade Commission Preliminary Report. May 16, 1975.

13. Chemical Economics Handbook. Stanford Research Institute. January 1974.

14. Survey Reports on Atmospheric Emissions from the Petrochemical Industry, Volume I. U.S. Environmental Protection Agency, Report No. EPA-450/3-73-005a. January 1974.

15. Survey Reports on Atmospheric Emissions from the Petrochemical Industry, Volume II. U.S. Environmental Protection Agency, Report No. EPA-450/3-73-005-C. April 1974.

16. Chemical Profile, Adipic Acid, April 28, 1975.

APPENDIX A

ADIPIC ACID MANUFACTURERS[16]

		Annual capacity,* million pounds
Allied Chemical Corporation	Hopewell, Virginia	25
Celanese Corporation	Bay City, Texas	140
DuPont	Orange, Texas	300
DuPont	Victoria, Texas	350
El Paso Natural Gas Company	Odessa, Texas	80
Monsanto	Luling, Louisiana	60
Monsanto	Pensacola, Florida	620
	Total	1575

*As of April 1975.